

Toxic Substances from Coal Combustion - A Comprehensive Assessment

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Introduction

The Clean Air Act Amendments of 1990 identify a number of hazardous air pollutants (HAPs) as candidates for regulation. Of the 189 substances identified as HAPs by Title III of the 1990 Clean Air Act Amendments (CAAA), 37 species, including 11 metals, have been detected by the Electric Power Research Institute (EPRI) in the flue gases of pulverized coal-fired utility boilers. Should regulations be imposed on HAP emissions from coal-fired power plants, a sound understanding of the fundamental principles controlling the formation and partitioning of toxic species during coal combustion will be needed. Over the past decade, a large database identifying the partitioning and emitted concentrations of several of these species has been developed. Laboratory data have also been generated to help define the general behavior of several elements in combustion systems. These data have been used to develop empirical and probabilistic models to predict species emissions.

While useful for providing average emissions of toxic species, these empirically based models fail when extrapolated beyond their supporting database. This represents a critical gap; over the coming decades, new fuels and combustion systems will play an increasing role in our nation's power generation system. For example, new fuels, such as coal blends or beneficiated fuels, new operating conditions, such as low-NO_x burners or staged combustion, or new power systems, such as the low-emission boiler system (LEBS) and high-efficiency power plant (HIPPS) being developed under the DOE sponsored Combustion 2000 programs and integrated gasification combined cycle (IGCC), are all expected to play a role in power generation in the next century.

The need for new predictive tools is not limited to new combustion systems, however. Existing combustion systems may have to employ controls for HAPs, should regulations be imposed. Testing of new control methods, at pilot and full scale, is expensive. A sound understanding of the chemical transformations of both organic and inorganic HAPs will promote the development of new control methods in a cost-effective manner. To ensure that coal-fired power generation proceeds in an environmentally benign fashion, methods for the prediction and control of toxic species in a broad range of coal fired systems must be developed.

Objective

In this program, a team led by Physical Sciences Inc. (PSI), and involving researchers from the University of Kentucky, USGS, MIT, the University of Arizona, the University of Connecticut, and Princeton University are conducting a detailed research program with three major objectives: (1) to elucidate the important mechanisms of toxics formation and partitioning; (2) to develop submodels for the appropriate trace toxic species transformations; and (3) to incorporate these mechanisms into an Engineering Model to predict trace toxic formation, partitioning, and fate based upon coal and combustion parameters.

In the two-year Phase I program described here, preliminary experiments were performed to decide upon the relevant mechanisms for trace element transformations. The three-year Phase II program which follows will contain more detailed experiments and model development activities.

Approach

We chose four coals for detailed study in Phase I. Variation in source and coal mineralogy were criteria for selection, as well as economic importance. The four coals are as follows:

- ▶ Pittsburgh Seam: Northern Appalachian bituminous coal;
- ▶ Elkhorn and Hazard Seams: Eastern Kentucky, low sulfur, “compliance” coal;
- ▶ Illinois 6 Seam: Illinois basin bituminous coal;
- ▶ Wyodak Seam: Powder River Basin sub-bituminous coal.

Pulverized samples were procured and characterized by traditional analyses as well as advanced analyses such as Computer-Controlled Scanning Electron Microscopy (CCSEM), Mössbauer spectroscopy, and X-Ray Absorption Fine Structure (XAFS) spectroscopy at the University of Kentucky and selective leaching and microprobe at USGS. Of particular interest were the forms of occurrence of the trace elements Hg, As, Se, and Cr in the coals. All experimentalists in the program received samples from the same lot of pulverized coal.

This project employs three types of experiments that isolate the important transformation steps for study as much as possible, while retaining the conditions typically present during coal combustion, with a fourth that approaches realistic utility pulverized coal combustion and allows for examination of all mechanisms simultaneously. Experiments were conducted on the following apparatus: (1) fundamental *bench scale studies*, using equipment such as a fixed bed reactor to isolate gas phase reactions and gas-solid reactions; (2) *drop tube experiments*, which allow exposure of narrowly size and density classified particles under flow and heat treatment conditions which are closer to realistic condition for evaluation of condensation and of condensed-state reactions; (3) *integrated combustion experiments*, conducted in a larger scale (0.25 kg/h) laboratory combustor, that use utility grind coal samples and employ realistic combustion stoichiometries from reducing conditions through to fully oxidizing for evaluation of excluded mineral effects and combustion effects; and (4) *larger scale combustion experiments*, using a continuous 100,000 Btu/h coal-fired combustor that maintains realistic heating and cooling rates and permits examination of trace toxics partitioning when *all* of the important mechanisms are contributing simultaneously.

Results

Forms of Occurrence of Trace Elements in Coal Table 1 summarizes the results to date regarding the form of occurrence. The information in the table is based on XAFS, Mössbauer, and selective leaching analyses. Se, As, and Hg are frequently associated with pyrite grains in the coal, although not exclusively. Other mineral associations or organic associations were also

observed as described below.

Arsenic was almost entirely associated with pyrite in the three bituminous coals, although a significant amount of the pyrite (and arsenic) in the Elkhorn/Hazard coal appeared to have been oxidized. In the Wyodak coal, the arsenic appeared to be organically associated.

Table 1. Forms of occurrence of selected trace elements in Phase I coals

	Pittsburgh	Illinois 6	Elkhorn/Hazard	Wyodak
Arsenic	mostly pyrite	mostly pyrite	mostly pyrite, some oxidized or in fine grains	organically associated
Selenium	all pyrite	pyrite and organically associated	pyrite and organically associated	<i>analyses in progress</i>
Mercury	mostly organic, some sulfides	organically associated	organically associated, some sulfides	<i>analyses in progress</i>
Chromium	CrOOH and clay minerals	mostly CrOOH, minor clay minerals	CrOOH, chromite, minor clays	organically associated

Selenium was almost completely associated with pyrite in the Pittsburgh coal, but split between pyrite and an organic form in the Illinois 6 and Elkhorn/Hazard coals. Determination of the form in the Wyodak coal is still in progress. Mercury is commonly associated with the organic fraction of the coal, although the presence of mercury in sulfides was noted for the Pittsburgh and Elkhorn/Hazard coals.

The association of chromium varies widely among the four coals. In all the bituminous coals, a significant fraction of the chromium is associated with an amorphous CrOOH phase which may be finely divided crystals in the coal. In the Illinois 6 coal, chromium is almost entirely associated with the phase, while in the Pittsburgh and Elkhorn/Hazard coals other forms of chromium, in clays or oxides, were observed in addition. In the Wyodak coal, an organic association is indicated for chromium.

Vaporization of Trace Metals in the Flame Data were obtained on the vaporization of trace elements in the flame zone at two facilities: MIT's drop tube furnace (DTF) and PSI's entrained flow reactor (EFR). Coals burned in the DTF were classified by size and then by density. The size classification allows fundamental kinetic information on vaporization to be determined. The density classification provides data on the behavior of different forms of minerals in coal (i.e., high

pyrite concentration versus low pyrite concentration) while keeping the other coal properties the same. By varying the oxygen content in the DTF experiments, different particle temperatures were obtained during combustion. The resulting data on trace element vaporization as a function of particle temperature and size will be incorporated into a fundamental kinetic model. Utility grind samples were burned in the EFR at realistic stoichiometric ratios. The ash was sampled at high temperature, giving a snapshot of the vaporization behavior in a flame which more closely resembles real-world conditions. Comparison of the EFR results with the DTF results highlights the strong effect of char particle temperature on vaporization of all trace elements.

Based on the combustion data generated in Phase I, we can make preliminary conclusions about the effect of the form of occurrence of three trace elements (As, Se, and Cr) on their behavior in the combustion zone. The behavior of mercury was assumed to be independent of form in the coal due to the high volatility of mercury in the flame and to existence of only one gaseous form at high temperatures; all mercury was assumed to vaporize in the flame zone.

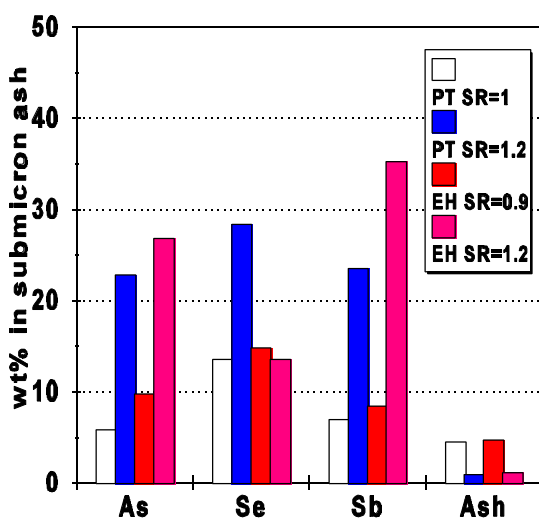


Figure . Figure 1. Amount vaporized under oxidizing and reducing conditions in the EFR for Pittsburgh (PT) and Elkhorn/Hazard (EH) coals.

decrease in vaporization under sub-stoichiometric conditions, while selenium did not, except for the Pittsburgh coal in which all the selenium was pyritically associated.

The form of selenium in the coal did not seem to have a major impact on its vaporization behavior. One minor effect was noted, however. Selenium associated predominantly with pyrite appeared to be less volatile under reducing conditions than under oxidizing conditions. For coals with a mixture of organically associated selenium and pyritically associated selenium there was little difference in vaporization as a function of flame stoichiometry. Figure 1 compares vaporization of selected trace elements (and ash) for the Pittsburgh and Elkhorn/Hazard coals burned at oxidizing and reducing conditions in the EFR. The char particle temperature is expected to be similar for oxidizing and reducing conditions in this furnace. Thus, we expect that differences observed are due to differences in combustion environment rather than particle temperature. Arsenic and antimony showed a pronounced

The form of arsenic does not seem to affect the vaporization in the flame, and hence the partitioning of As between large and small ash particles. Figure 2 shows the amount of arsenic in the submicron ash as a function of the arsenic content of the coal from the data generated in the DTF on size and density-segregated coal particles burned in 20% oxygen at 1500 K. Note that there are multiple points for each coal corresponding to different initial size and density fractions.

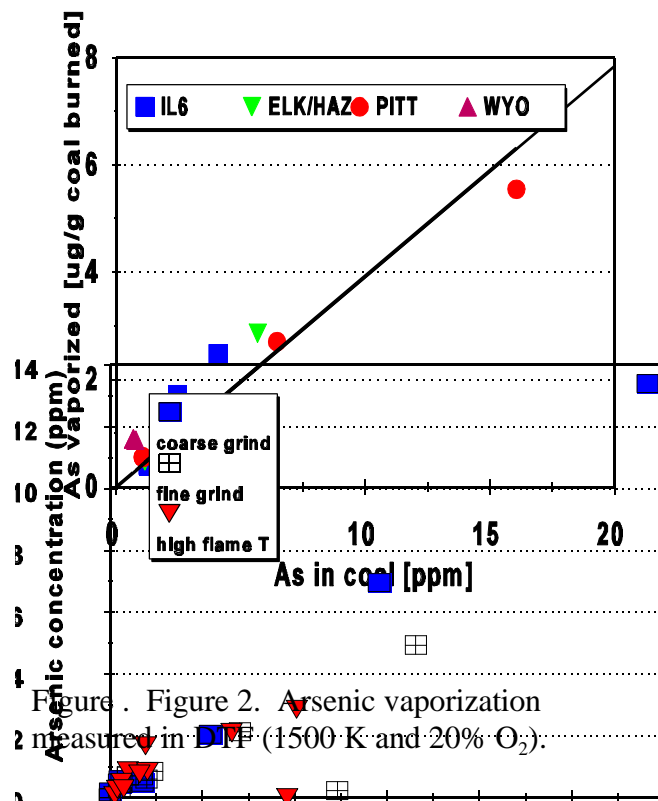


Figure . Figure 2. Arsenic vaporization measured in DTF (1500 K and 20% O₂).

The form of chromium in coal seemed to have some effect on the amount of chromium vaporized in the flame zone. Coals with predominantly organically associated Cr showed higher vaporization of chromium in the flame zone as compared to those with a mixture of forms. Figure 3 shows data obtained from the DTF on the amount of Cr in the submicron ash versus chromium content in the coal. Two coals, Illinois 6 and Wyodak, had predominantly organically-associated chromium. Data for these two coals are shown in open circles and lie above the line for the other two coals, Pittsburgh and Elkhorn/Hazard, which contained a mixture of organically and mineral-associated chromium.

Post-Combustion Transformations of Trace Elements Pilot scale data were obtained from two facilities which provide insight into the mechanisms for post-combustion transformations of key trace elements. The

The data generally lie on a straight line, indicating that the form of arsenic in the coal is not important in determining vaporization under these conditions.

Coal oxidation or weathering did not significantly affect the vaporization of arsenical pyrite. Experiments were conducted on an Illinois 6 coal sample which was artificially weathered. The oxidation of pyrite in the sample was followed using Mössbauer analysis. Combustion experiments were performed in the EFR at a stoichiometric ratio of 1.2 using a fresh sample and a weathered sample. About 50% of the pyrite in the weathered sample had oxidized. Over 50% of the arsenical pyrite in the sample was oxidized to arsenate, as determined by XAFS. No effect of weathering was observed on the amount of arsenic vaporized during combustion.

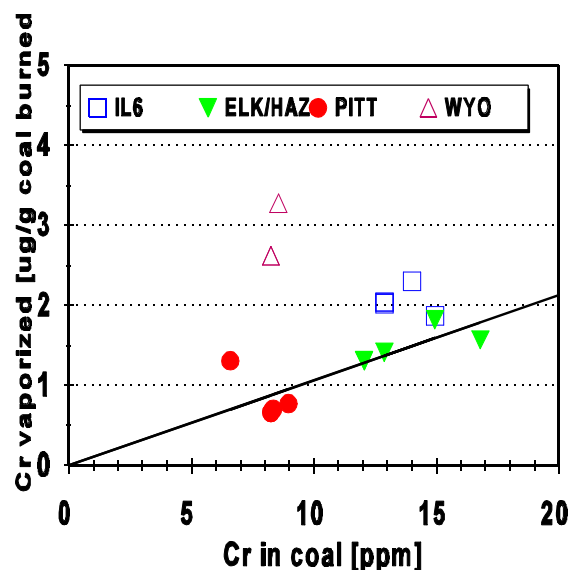
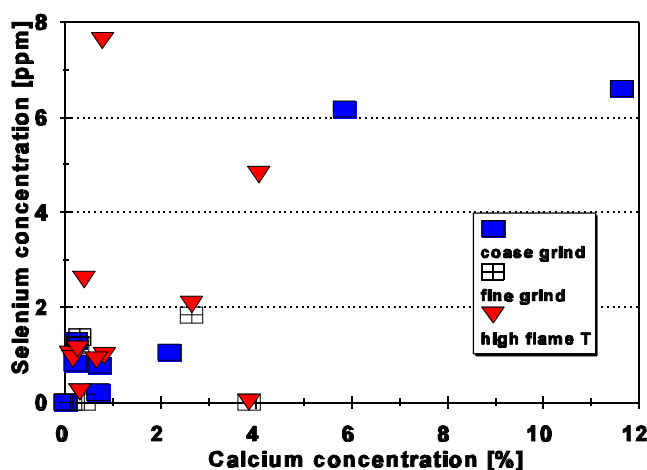


Figure . Figure 3. Chromium vaporization measured in DTF (1500 K and 20% O₂)

Wyodak coal was burned at ABB-Combustion Engineering's FPTF combustor. Ash samples were taken at the inlet of a pilot-scale ESP using the Berner Low Pressure Impactor (BLPI) to obtain detailed compositional information of submicron particles. The effects of coal grind and flame temperature on trace element concentration in the submicron were probed. Coal grind did not have an effect on vaporization of bulk ash or trace elements. The flame temperature, however, had a pronounced effect on vaporization. Vaporization of arsenic and selenium, as well as other elements such as antimony, increased with increasing flame temperature. A substantial increase in the retention of mercury in the submicron ash was also noted for the high flame temperature case.

The pilot scale data also show the interaction of calcium with the trace elements As and Se. The Wyodak coal is high in calcium. Figure 4 shows the correlation between calcium content of the ash and arsenic or selenium content. Since the BLPI was used to collect size-segregated ash samples, there are many different size cuts for each condition under which the coal was burned. As Figure 4a indicates, there is a strong association in the ash with calcium and arsenic, indicating the possible formation of a calcium arsenate. This association is not observed in the DTF or EFR data. Thus we conclude that calcium arsenate forms in the post-combustion region. The correlation between calcium and selenium (Figure 4b) was not as strong, particularly for the high flame temperature experiment. This may be due to the higher volatility of selenium relative to arsenic.

The Illinois 6 and Pittsburgh coals were burned at the University of Arizona's Pilot Scale Combustor System with a stoichiometric ratio of 1.2. The BLPI was again used to obtain detailed information on the submicron ash particles. Sampling was conducted at two temperatures, approximately 1150°C and 840°C, which allows us to observe the growth of the submicron aerosol as the flue gases cool. For both coals,



4b

Figure .

Figure 4. Composition of Wyodak ash measured at inlet to pilot-scale ESP as a function of combustion conditions for (a) As vs. Ca and (b) Se vs. Ca.

the growth of the submicron aerosol as the flue gases cool. For both coals, the growth of the submicron aerosol is clearly observed as Figure 5 illustrates. Analysis of trace element composition as a function of particle size will provide insight into the interaction of trace elements and fly ash as the flue gases cool.

Since mercury appears to be the most important trace metal in terms of its impact on the environment, we have focused some of our effort on increasing the state of understanding of mercury partitioning and speciation. Although combustion produces elemental mercury at flame temperatures, coals typically contain sufficient chlorine to oxidize a

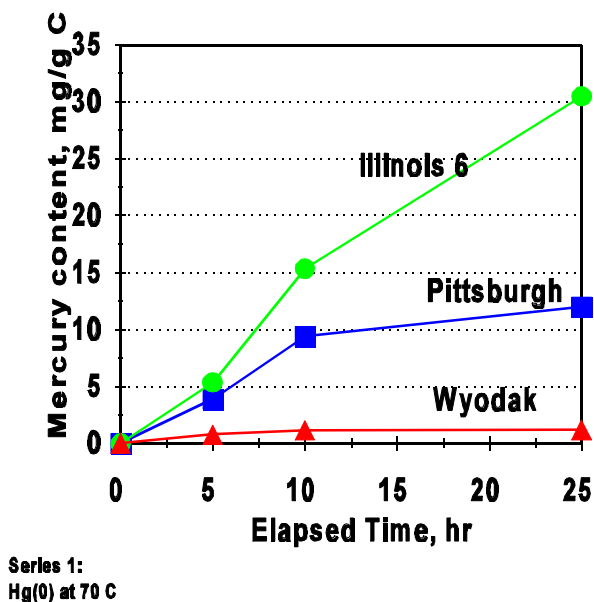


Figure 6. Adsorption of elemental mercury by char samples in UoA fixed bed reactor at 70°C.

Figure 5. Mass particle size distribution for Pittsburgh coal at U of A pilot scale combustor at two different sampling ports: High (1150°C) and Low (840°C) Temperature.

While the carbon content of the ash has some effect on the adsorption of mercury, data on mercury content as a function of carbon content taken at the DTF show that carbon content alone is not a good predictor of mercury content. Several low carbon ash samples adsorbed large amounts of mercury. One possible hypothesis to explain these results is the formation of soot in the DTF which would condense on fly ash and form a high surface area mercury sorbent.

portion of the elemental mercury to HgCl_2 at temperatures in the range of 500-650°C (900-1200°F), according to equilibrium calculations. Examination of field data as well as preliminary experiments in the EFR suggest that the gaseous oxidation of mercury is “frozen” at some temperature in the range of 500°C to 550°C. There is evidence that reactions of other trace species in flue gas are also kinetically limited as the flue gas cools. For example, kinetic calculations for chlorine in flue gas indicate that approximately 1% of the chlorine is present as Cl_2 at ESP inlet temperatures (150°C to 200°C) while equilibrium predicts 30-50% as Cl_2 at those temperature.

Gaseous mercury species interact with flyash resulting in the conversion of elemental mercury to an oxidized form (presumably $\text{HgCl}_{2(g)}$) and the adsorption of a significant portion of the mercury on the particulate

Because a better understanding of mercury-carbon interactions is needed, the University of Arizona carried out bench scale experiments in which chars prepared from the program coals were exposed to vapor-phase mercury. The amount of mercury adsorbed by the chars was measured as a function of time. Figure 6 shows the data obtained at a bed temperature of 70°C using elemental mercury in a simulated flue gas composition. The mercury content of the char has been normalized to the carbon content of the char. As the figure shows, chars from the Pittsburgh and Illinois 6 coals were shown to have much higher affinities for elemental mercury than a char from the Wyodak coal, in spite of the fact that the Wyodak char had as much or more carbon as the bituminous chars. Char surface area was also not correlated with mercury adsorption. This indicates that there are other properties of the char which are important for mercury adsorption.

Work was also initiated to better understand the forms of adsorbed mercury on carbon materials. The University of Kentucky analyzed a series of carbon-based sorbents which had been exposed to mercury in simulated flue gas in a bench scale reactor at the University of North Dakota Energy and Environmental Research Center. Figure 7 shows an example of XAFS spectra of mercury obtained from these sorbents. Preliminary results indicate that the composition of the flue gas affects the amount of mercury adsorbed, but not the form of mercury on the surface. The sorbents were in some cases doped with compounds designed to react with mercury. The dopants were observed to have an effect on the form of mercury in the solid. The form of mercury in a iodine-doped activated carbon was distinct from that of a sulfur-doped carbon or undoped activated carbon. Further refinements of this analytical technique are expected to greatly increase our understanding of the behavior of mercury in the Phase II program.

Field Data on Toxic Emissions A detailed examination of the available coal-fired power plant field data was conducted. Data reviewed included EPRI and DOE-sponsored studies as well as data from the scientific literature. Review of data on organic emissions highlighted the need for a better identification of the species, both carcinogenic and mutagenic, that may be present in coal-fired power plant emissions. Concerns were raised about the short list of species which were analyzed and the lack of mass balance closure on the analytical measurements.

Based on a review of available field data on inorganics, we prioritized the 11 trace metals identified as Hazardous Air Pollutants in the 1990 Clean Air Act Ammendments relative to work in the Phase II program: Highest Priority - Hg, Se, As; Moderate Priority - Cd, Sb, Ni; Low Priority: Cr, Co, Pb, Be, Mn.

The low priority elements are those for which the behavior is already well predicted, based on a comprehensive review of EPRI and DOE field data discussed in the Final Report. In particular, these elements show uniformly high capture efficiency in all types of air pollution control devices (APCDs) studied to date. Not only is the capture efficiency for the element high, but it falls within two standard deviations of the average particulate matter capture efficiency for the particular device. While emission of these elements may be important from a human health risk perspective, further fundamental study is not deemed necessary because emissions are already well-correlated with overall particulate

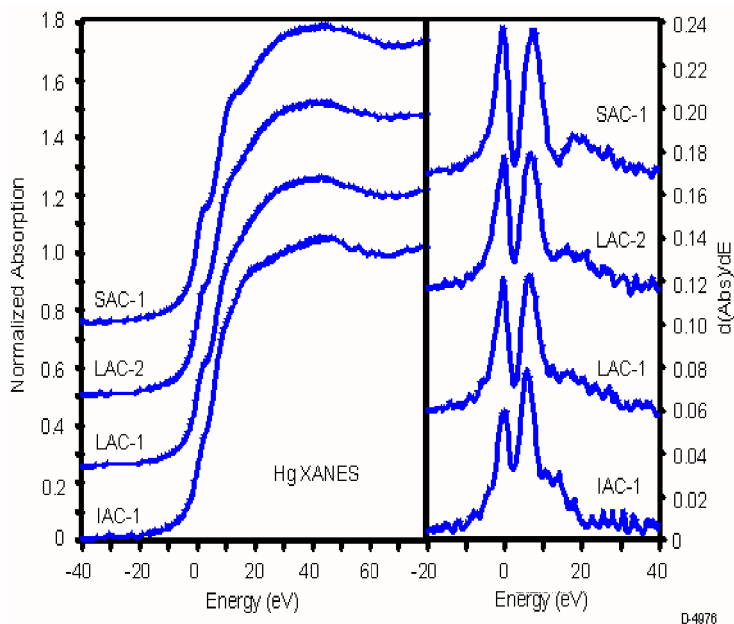


Figure . Figure 7. XAFS spectra (left) and first derivative (right) of lignite activated carbon (LAC), sulfur-doped activated carbon (SAC), and iodine-doped activated carbon (IAC)

matter collection efficiency.

Three elements, Cd, Sb and Ni were judged to be moderate priority. While concentrations of Cd in coal are typically low, this element is toxic. The field data show that capture efficiencies for Cd in ESP's averaged 94%, less than the total particulate capture efficiency. This leads us to speculate that there is a substantial amount of Cd in the fine particulate. Furthermore, when looking at data for sub-bituminous coals alone, the average capture rate for Cd is only 92%. If this is statistically significant, there may be some effect of coal composition on Cd disposition in the flue gas. In the case of Sb, there were insufficient field data to draw a conclusion about the emission as a function of coal type or APCD. Antimony is a volatile element, one which tends to escape collection in APCD devices. The emission of nickel in field studies showed poor correlation with ratio of the coal Ni content to total particulate matter capture efficiency. Furthermore, Ni emissions from sub-bituminous coal showed low capture efficiencies relative to the total particulate matter capture efficiency, although the Ni capture efficiencies averaged 96% in this case.

The field data on As emissions show variability from one facility to another. A few plants had low As capture (72-85%). Furthermore, the matter of As speciation has not been put to bed yet. In the ambient atmosphere, a 50-50 mixture of As^{+5} and the more toxic As^{+3} has been detected in particulate matter. Measurement of As speciation from larger scale facilities is warranted. In the flame and post-combustion gases, As is both volatile and reactive with compounds in the ash such as calcium as pilot-scale data from ABB demonstrate. We have preliminary evidence that the composition of the ash is important in determining both the vaporization rate of As and the final rate of retention in the ash. Further work on the relationship between the form of As in the coal and its volatility in the flame is warranted as well as work on capture rates and speciation in the fly ash post combustion. Selenium is a volatile element in the flame and shows low capture efficiencies in coal-fired power plants. The form of Se in the coal does not seem to affect the volatility during combustion. However, the composition of the ash seems to exert a major influence on the emission of Se from power plants. Average capture efficiencies were strongly dependent on coal type: 98%, sub-bituminous coals; 62%, lignites; 44%, bituminous coals. This points to an interaction between selenium and calcium in the large fly ash particles in sub-bituminous coals and lignites consistent with the pilot scale data for the Wyodak coal.

Application

The new Toxics Partitioning Engineering Model (ToPEM) will be applicable to *all* combustion conditions including new fuels and coal blends, low- NO_x combustion systems, and new power generation plants. Development of ToPEM will be based on PSI's existing Engineering Model for Ash Formation (EMAF). Since ToPEM will be a fundamental, mechanistic model, it will fill needs not met by existing models.

The PISCES model is one such model which has been developed by EPRI. This model allows utilities to estimate the emissions of HAPs from fossil fuel-fired power plants and to evaluate the effect of various control strategies for HAPs. The PISCES power plant model performs mass and energy balances on all major streams in the power plant: gas, liquid and solid. For estimation of trace metal emissions (in all media), the PISCES model employs a database which provides partitioning of chemical species in each subsystem of the power plant. The database is based on field measurements in the open literature and in the reports of the DOE and EPRI-sponsored field studies.

Prediction of the partitioning and speciation of trace metals from power plants by the PISCES model depends on the quality of the data in the database. For many of the HAPs, the existing database seems to provide a reliable prediction of emissions. For certain elements such as Hg, As, and Se, however, this is not the case as discussed in more detail below. Furthermore, the database is comprised of measurements from a limited number of fuels and types of combustion systems. Extrapolating to new fuels and blends or to new combustion systems will result in less accurate predictions. The Toxics Partitioning Engineering Model (ToPEM) under development in this program will address the limitations inherent in using a fixed database by supplying a fundamental model capable of adapting to new fuels and new combustion conditions.

Future Activities

We conclude that a database approach will not be accurate for prediction of Hg, Se, As, and Cd emission rates from coal-fired power plants. A more fundamental approach, based on the chemistry of the element and the conditions in the flue gas, will be required. In the Phase II program, we will focus on Hg, Se, and As partitioning and speciation in the flue gas. As in the Phase I program, we will use a variety of combustion scales, from single particle to self-sustained combustion, and advanced analytical methods to understand the trace element transformations. We also plan a small, but fundamental, effort on the kinetics of soot formation from coal combustion that should help understand the conditions under which toxic organic emissions are likely to form.

In the Phase II program, PSI will work with EPRI to turn the results of our research into models that can augment the existing PISCES model. Specifically, as part of the Phase II program, we will add new submodels to the existing mineral matter transformation models for i) vaporization of trace elements during combustion as a function of combustion conditions and coal properties; ii) condensation of vapor phase trace elements post combustion; iii) speciation and partitioning of mercury post combustion.

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